ANL-6377
Engineering and Equipment
(TID-4500, 16th Ed.,
Amended)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois

PROCESS VESSEL DESIGN FOR FROZEN-WALL
CONTAINMENT OF FUSED SALT

by

R. W. Kessie, J. D. Gabor, W. J. Mecham,
and A. A. Jonke

Chemical Engineering Division

August 1961

Operated by The University of Chicago
under
Contract W-31-109-eng-38

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I. ABSTRACT

The feasibility of the containment of a molten sodium fluoride-zirconium fluoride salt at 550 C in vessels with a protective inner liner of frozen salt of the same composition was demonstrated. Two different designs were used for supplying internal heat directly to the molten salt: induction heating and electrolytic heating. The test equipment was of a size practical for processing zirconium-uranium alloy reactor fuel by the Fused Salt Process.

II. SUMMARY

The containment of a fused sodium fluoride-zirconium fluoride mixture in a process vessel using the frozen-wall principle to prevent corrosion of the vessel wall was demonstrated. Two designs were tested, employing different electrical means of internally heating the fused salt while cooling the outer part of the container.

In one method, direct heating of the fused salt was provided by magnetic induction from a 450-kc oscillator. No contact of metal with the fused salt is entailed in this mode of heating, and all metal components of the system were kept well below the melting point of the salt (ca 550 C). An array of water-cooled nickel tubing was used to cool the frozen salt layer, thereby preventing the fused salt from contacting the induction coil. The configuration of the coolant tubes was such that interference with the magnetic induction field was negligible.

A design using electrolytic heating was also demonstrated. Current flowing between two salt-immersed electrodes heated the fused salt directly, and the frozen salt wall was maintained at the water-cooled vessel wall. The electrodes incorporated special features to promote uniform salt heating, and to allow startup with a solid salt charge. The sparge lines were made integral with the electrodes to minimize the number of components in contact with the salt.

Practical ranges of the size of salt charge, depth of fused salt, and sparge gas rates were used. Nearly uniform frozen-wall thicknesses of about one inch were obtained. The heat flux was found to be the major factor in controlling wall thickness.

III. INTRODUCTION

In the Fused Salt Fluoride Volatility Process for recovery of uranium from zirconium-uranium alloy reactor fuel, the alloy is dissolved in a fused fluoride mixture by sparging with hydrogen fluoride and then the uranium is recovered as the hexafluoride by sparging with fluorine. A schematic diagram of the process is shown in Figure 1. The chemical feasibility of this process has been demonstrated.^(1,2)

Figure 1

Fused Salt Process for Recovery of Uranium Hexafluoride from Zirconium-Uranium Alloy Reactor Fuel

The chief practical problem in this process, however, is the rather severe corrosion of the metal containers by the molten salt, which removes the protective fluoride film from the metal. One method of overcoming this corrosion is to cool the container wall sufficiently to freeze a thin wall on the inside of the vessel, thereby preventing direct contact of the metal with the molten salt phase. In this system, an internal source of heat must be provided to keep the bulk of the salt molten, and proper control of heating and cooling is required.

This study concerns the adaptation of induction heating and electrolytic heating as a means of furnishing this internal source of heat to

maintain thin, uniform, and stable frozen-wall protection of the containment vessel. In both the induction and electrolytic methods, heat is generated directly in the molten salt phase by electrical currents. This mechanism is highly efficient for frozen-wall operation because the frozen salt is a good electrical insulator and picks up a negligible amount of heat. This property of the salt also allows the resistance across the frozen salt protective layer to serve as a means of monitoring the thickness of the protective layer.

The salt used in these tests was 40 mol percent zirconium tetrafluoride and 60 mol percent sodium fluoride. Relevant physical properties of the salt⁽³⁾ are given in Table 1.

Table 1

PROPERTIES OF A FLUORIDE MIXTURE
(ORNL-2150)

Mixture	Component	Mol %	Wt %	Average Molecular Weight	Liquidus Temp
30	NaF	50	19.01	110.5	520 C
	ZrF ₄	46	69.62		
	UF ₄	4	11.37		
<u>Density</u>					
Solid at Room Temperature (g/cc)				4.09 ^a	
Liquid (ρ = g/cc, T = C)				ρ = 3.93 - 0.00093T	
Liquid (ρ = lb/cu ft, T = F)				ρ = 246.3 - 0.0322T	
Mean Volumetric Coefficient of Liquid Expansion (1/C × 10 ⁴)				2.84	
<u>Enthalpy, Heat Capacity, and Heat of Fusion</u>					
<u>Solid (340 - 500 C)</u>					
Enthalpy (cal/g)			H _T - H(0 C) ^a = -12.6 + 0.215T		
Heat Capacity [cal/(g)(C)]			c _p ^a = 0.22		
Heat Capacity at 300 C (572 F)			c _p ^a = 0.22		
<u>Liquid (540 - 894 C)</u>					
Enthalpy (cal/g)			H _T - H(0 C) ^a = 2.1 + 0.3178T - 4.28 × 10 ⁻⁵ T ²		
Heat Capacity [cal/(g)(C)]			c _p ^a = 0.3178 - 8.56 × 10 ⁻⁵ T		
Heat Capacity at 700 C (1292 F)			c _p ^a = 0.258		
<u>Heat of Fusion</u> (cal/g)			H _L - H _S ^a = 57		
<u>Thermal Conductivity</u>					
K [BTU/(hr)(ft)(F)]			0.5 (Solid slab)		
			1.3 (Liquid)		
<u>Viscosity</u>					
Temp, (C)	Viscosity (Centipoises)				
600	8.5 ^a				
700	5.4 ^a				
800	3.7 ^a	Exponential Form μ (centipoises) = 0.0981e ^{3895/T,K}			
850	3.2 ^a				
<u>Prandtl Number</u> : 4.4 at 593 C; 2.5 at 704 C; 1.6 at 816 C					
<u>Electrical Conductivity</u> (ohm-cm) ⁻¹ : 0.87 at 593 C; 1.16 at 704 C; 1.45 at 816 C					
<u>Surface Tension</u> (dynes/cm): 157 at 530 C; 132 at 630 C; 115 at 730 C					

^aDenotes experimental values. Other values given are calculated or estimated.

The general objective of this study was to develop practical designs suitable for process use, in which molten salt charges in the range from 100 to 1000 lb could be dependably contained by a thin frozen wall while being sparged with fluorinating gas.

IV. INDUCTIVELY HEATED FROZEN-WALL VESSEL DESIGN

Induction heating is unique in that it makes possible the holding of a fused salt charge in a container of its own solid phase, without contacting any foreign material. This is most important for processes where the purity of the material is of paramount interest. For the present process application, however, downlines for sparge gas and for salt removal are required, and these components are difficult, if not impossible, to protect from contact with the molten salt. But in any case induction heating is the only method which requires no salt-wetted components for internal heating, and therefore allows use of the minimum number of components in contact with the salt.

A. Principles of Induction Heating

A changing magnetic field generates voltage gradients in any region it penetrates. In a material of high electrical conductivity the resulting induced currents will oppose changes in the field. This opposition limits penetration of a changing or oscillating magnetic field and thereby excludes the field from the inside of the conducting body. A measure of the penetration into a body from the surface is given by the penetration factor $p^{(4)}$:

$$p(\text{cm}) = \sqrt{\frac{10^9 \rho}{8\pi^2 \mu f}}$$

where

ρ = electrical resistivity of the material, ohm-cm;

μ = magnetic permeability of the material;

f = frequency of the electromagnetic field, cycles/sec.

Heat is generated in the material by the current induced by the oscillating magnetic field. If the dimensions of the material are greater than the penetration distance, the magnetic field entering the surface of the conductor interacts and is in effect absorbed, and a corresponding amount of heat is produced.

The magnetic field and the corresponding induced current both decrease with increasing penetration distance inside an electrical conductor.

This is illustrated in Figure 2, drawn on the basis of an exponential reduction in which the penetration factor p is the distance giving a reduction in current by the factor $1/e$, or 0.36.

Figure 2

Effect of Penetration of an Oscillating Magnetic Field into a Conducting Material on Current and Heating Density

Heating density is proportional to the square of the current density and therefore decreases at twice the rate of the current density with respect to the distance from the surface. In terms of Figure 2, the heating density has decreased by a factor of $1/e$ over a distance of one-half p . The total heat input is equal to the rate of heat generation per unit volume at the surface multiplied by the product of the surface area times one-half p . The rate of surface heating cannot exceed the rate of change of total energy per volume in the oscillating magnetic field. Neglecting nonuniformities in the magnetic field, the rate of change of total energy in the magnetic field is given by the product of volts and amperes in the work coil divided by the coil volume.

The analysis presented in the above two paragraphs is valid only if p is small compared with the size of the load. When the load dimension becomes 2 to 4 times p , the heat generation in the load is a maximum, due to optimum absorption of energy.

As p becomes larger than the dimension of the body heated, the load no longer excludes the magnetic field and no longer absorbs its energy effectively. It then approaches the characteristics of electrical non-conductors, which have relatively large values of ρ and p . For this case, the heating effect decreases as p increased, the heating being proportional to $1/p^2$.

The above approach is particularly helpful in understanding the present application, because the major heating effect takes place in the material of intermediate resistivity. The resistivities of the material used in the experimental work are given in Table 2, along with the value

of p at 400 kc. Thus, with the materials used and with dimensions in the range from $\frac{1}{4}$ to 12 in., the molten salt will be the only material to be heated at a significant rate.

Table 2

MATERIAL PARAMETERS IN INDUCTION-HEATING TESTS

	Resistivity ρ (ohm-cm)	Penetration Depth p , for 400 kilocycles (in.)	Optimum Dimension $3p$ (in.)
Frozen Salt (50 m/o NaF, 50 m/o ZrF ₄)	10^8	22,000	66,000
Molten Salt	1	2.2	6.6
Stainless Steel	7×10^{-5}	0.021 ^a	0.063
Nickel	10^{-5}	0.0071 ^a	0.0213
Copper	2×10^{-6}	0.0031	0.0093

^aCalculated for $\mu = 1$, since, in general, μ will depend on magnetic field strength.

Configuration is another basic factor affecting the design. For the most practical case in which the charge is surrounded by the work coil, the closer the coil is to the charge, the higher is the overall efficiency of power generation. However, the temperature control must be such that molten salt does not contact the coil, which would result in a short circuit. In order to get high coupling efficiency and yet have positive protection against short circuits, cooling should be provided between the induction coil and the salt charge, that is, a cooling means should be located inside the induction coil. This cooling component should not, however, be such as to shield or absorb the magnetic field, nor should it be so bulky as to give an unfavorable size. These factors were considered in the equipment design.

B. Description of the Equipment⁽⁵⁾

The experimental frozen-wall vessel is shown in a top view in Figure 3. It consists of an alundum crucible, 12 in. OD by 18 in. high, with $\frac{1}{2}$ -in.-thick sides and bottom. The cooling coils, fabricated of $\frac{1}{4}$ -in.-OD nickel tubing and spaced $\frac{1}{2}$ -in. apart along the vertical wall, are on the inside wall of the crucible. Water is used as the coolant. The stainless steel secondary vessel is 20 in. OD by 24 in. high. The annulus between the crucible and secondary vessel is filled with tamped granules of expanded mica, which provide an electrical-insulating support for the induction coil.

Figure 3

Induction-heated Vessel for Frozen-wall Tests⁽⁵⁾

The configuration of the induction coil and of the internal cooling grid was developed for the specific purpose of this study. The desired arrangement involved the location of the cooling zone on the inside of the induction coil, being thus located between the source of electromagnetic power and the charge being heated. In this manner, close approaches of molten salt to the coil are prevented at all times. In order that the cooling means should not absorb power, it was made in the form of an array of tubes parallel to the lines of the induction field. The tubing array shown fulfilled these design requirements.

The radiofrequency source was an electron tube oscillator (model 1500 Ther-Monic) with a 15-kw output rating.

C. Selection of Induction Coil⁽⁵⁾

Preliminary experiments to select a suitable design of induction coil for coupling the oscillator to various sized loads in the test assembly were made with 40 weight percent sulfuric acid as a stand-in system. Data obtained for various load and coil configurations are shown in Table 3.

Table 3

INDUCTION-HEATING TESTS USING 40 w/o SULFURIC ACID⁽⁵⁾

Work Coil		Acid Charge ^a		Oscillator Plate		Transformer Current ^f		Coil Current ^b (amp)	Frequency (kc)	Heat Input ^c (kw)	Efficiency (%)	Estimated Heat Input ^d (kw)
Turns	Length (in.)	OD (in.)	Height (in.)	amp	kv	Primary (amp)	Secondary (amp)					
3	4	6	3.6	0.53	6.0	81	-	-	-	0.12	44	-
3	4	6	3.6	1.06	10.6	146	-	-	-	0.41	4	-
3	4	9	1.6	1.03	10.7	146	-	-	287	1.3	12	-
5	6	0	0	0.50	6.2	91	70	-	275	No load	-	-
5	6	9	9.8	0.66	5.8	85	66	-	275	3.5	25	-
5	6	9	9.8	1.28	10.7	-	113	-	-	-	-	-
3	6	0	0	0.48	5.3	92	128	-	290	No load	-	-
3	6	9	9.8	0.61	5.1	87	122	-	-	3.6	24	-
3	6	9	9.8	1.41	10.7	171	-	-	-	5.2 ^e	29	-
10	10	9	9.8	1.78	5.0	-	-	45	340	3.4 ^e	38	3.3
10	10	9	5.1	1.80	5.0	-	-	45	-	2.0	40	3.3
10	10	6	3.4	1.00	5.0	-	-	70	-	-	-	-
10	10	6	3.4	2.06	9.6	-	-	112	-	6.3	25	-
10	10	6	6.8	2.50	10.0	-	-	112	-	-	-	4.3
10	10	0	0	1.95	10.8	-	-	135	340	No load	-	-
5	5	0	0	1.90	9.5	-	-	156	415	No load	-	-

^aThe bottom of the acid charge was 1.5 in. above the bottom of work coil.

^bThe coil current was recorded for the direct-coupled cases and was equal to the secondary current when transformer coupling was used.

^cThis heat input was based on the heating of the load, i.e., the acid charge.

^dAn estimate of charge heating as suggested by Ther-monic is 70% of plate voltage times the change in plate current produced by adding the charge.

^eMaximum power input possible without overloading the model 1500 Ther-monic induction generator.

^f22-turn primary, 5-turn secondary, air core.

The acid solution had a resistivity of 1.3 to 0.8 ohm-cm from 30 to 60 C and thus matched the resistivity of the molten salt. The acid was placed in glass vessels sized and positioned to simulate the expected pool of molten salt. After making initial adjustments of the oscillator for coil and load, the oscillator was turned on for a measured interval of time and the temperature rise of the acid solution measured. Readings were taken without the acid at the same oscillator plate voltage (E_p) in order to verify the relation used for determination of power input to the load presented by the fused salt charge, namely,

$$P = 0.70 E_p \Delta I_p$$

In this equation, P is the power input, E_p is the plate voltage, and ΔI_p is the change in oscillation current produced by the load (acid charge). An attempt was made to use smaller coils with a 22- to 5-turn air-core transformer, but the coupling was poor (especially with charges of smaller diameter). On the basis of these experiments, it was decided to use a 5- and 10-turn coil directly coupled (no output transformer).

D. Fused Salt Tests ⁽⁵⁾

After charging solid salt, the unit was started by using tubular electric-resistance heaters to produce a small molten pool, about 4 in. OD by 5 in. high, in the center of the frozen salt. With a molten pool of this size, induction heating alone generated enough heat to enlarge the pool. In plant operation, startup could be accomplished by transferring molten salt into the unit from the dissolver or another vessel.

Direct observations of the salt wall were made and dimensions measured during operation. The operating conditions for the three runs are shown in Table 4.

Table 4

OPERATING CONDITIONS IN FROZEN-WALL INDUCTION-HEATED TESTS⁽⁵⁾

Mark I Test Assembly
Salt: 40 m o ZrF_4 -60 m o NaF

Run	1-1	1-2	1-3
Plate Input (kw)	10.7	23.0	7.8
Salt Input (kw)	-	5.5	1.25
Efficiency (%)	-	24	16
Wall Resistance (ohm)	2000	-	100,000
Coil Turns	10	5	5
Coil Length (in.)	10	5	5
Coil Current (rf amp)	65	125	95
Frequency (kc)	350	425	415
Minimum Wall Thickness (in.)	3.16	1.8	1.2
Bottom Wall Thickness (in.)	3.75	1.75	1.87
Wall Resistivity (ohm-cm)	-	-	$\sim 10^8$
Overall Average Wall Thickness (in.)	-	~ 0.75	~ 1.2
Heat Flux (kw/sq ft wall)	-	4.4	1.0

Thicknesses of the frozen walls are shown in vertical and in horizontal sections in Figure 4. The data were taken after conditions had stabilized for about one hour. Changing conditions from Run I-2 to Run I-3 required about one-half hour for the frozen wall to stabilize. From Figure 4 it can be seen that wall thickness varied inversely with power input. A 5-turn coil placed at the bottom of the charge appeared to be the best arrangement for this system. At no time in the tests did it appear that molten salt contacted the metal of the cooling coil. Measurements of the electrical resistance across the solid salt wall were taken to confirm this.

Figure 4

Frozen-wall Induction-heating Tests:
Cross Sections through Frozen Wall

In Run I-1, experiments made with and without sparging showed no appreciable effect of sparging on the frozen wall, except in the case where the sparge exit was close to the wall. In this case a local thinning of the wall was observed. Other effects of sparging were noted as follows:

a) With sparging, the melt temperature (525 C) was very uniform; without sparging, fluctuations (up to 85 C higher) of temperatures were noted. These fluctuations, due to convection currents, were random with position and time.

b) Without sparging, a thin crust was formed at the top of the melt. This crust was not over $\frac{1}{16}$ -in. thick and was periodically melted and re-formed by convection currents. A small gas sparge was sufficient to remove a crust already formed and to keep the molten surface clear of all frozen salt.

Once an initial stabilization had been reached at some power level, the system proved very stable over a wide range of power inputs and corresponding wall thicknesses, and did not require adjustments.

These tests indicate the feasibility of using induction heating for a frozen-wall fluorinator.

E. Design of Plant Equipment

A preliminary design for a remotely operated plant-scale unit is shown in Figure 5. All components except the salt lines should have a very long life, because no contact with fused salt is made. Two coils are shown in the figure; in normal operation only the bottom coil would be used. The long upper coil is for initial melting of a charge of solid salt. The initial startup of the vessel would use salt free of uranium and fission products. This would be charged to the maximum operating level and operated with the thinnest frozen wall in order to produce a stable wall. Before salt discharge, the heating power would be reduced to allow the wall to thicken. Process salt with uranium and fission products dissolved as fluorides would be charged at the same low-power setting used on discharge of the startup material.

Fluorine would be sparged until the uranium was volatilized as the hexafluoride. The power would be gradually increased while a small fluorine sparge continued in order to remove any last trace of uranium that may have become trapped in the frozen wall. Power would be reduced and the wall allowed to thicken before salt discharge. This increase in wall thickness during normal operation need only be sufficient to prevent uranium pickup by the molten salt from the frozen wall between the end of the fluorination and the salt discharge. Operation with the thinnest frozen wall would probably be reserved for decontamination with fresh salt and could be performed so that the frozen wall was reduced in thickness with each clean wash of molten salt. Each wash could be fluorinated for uranium recovery before discharge, if desired.

A major decision in the design of an inductively heated fluorinator unit concerns the internal coolant grid (inside the induction coil). The heat load for a stable wall operation is of the order of one kw/sq ft wall area. Designs involving a gas coolant require large volumetric flows, high areas, and high pressure; these features are undesirable. Possible liquid coolants are water, organics, fused salts, or liquid metals. Heat transfer with any of these is no problem, and the chief question concerns safety in the case of a leak of coolant into the fused salt.

Figure 5

Design for a Remotely Operated Plant-scale Frozen-wall Fluorinator

From this standpoint, NaK is favorable as a coolant. It is not subject to thermal decomposition, needs no heating to start flowing in pipes, and in the event of a leak does not introduce any foreign material into the salt or off-gas system. Its vapor pressure at process temperature is below one atmosphere. The reaction with salt is negligible and with fluorine gives no volatile products. The absence of vapor-producing reactions minimizes the source of explosions. The only potential problem with the fluorine reaction is the heat generated. However, the amount of fluorine available for immediate reaction is small, only a few cubic feet in the fluorinator vapor space. The heat capacity of the metal vessel enclosing the vapor space is such as to limit the temperature rise (due to this amount of fluorine reacting) to less than 100 C.

The salt-transfer lines were $\frac{1}{2}$ -in. schedule 40 Inconel pipe. During salt transfer, they were heated to 600 C by passing 500 amp of 60-cycle alternating current through the pipe. The voltage required is 1 volt/ft. At this power level no insulation is required to allow the pipe to heat to 600 C. The absence of insulation in the pipes has the result that the temperature along the pipe, even at bends, is very uniform. The major heat loss is by radiation.

In order to prevent salt freezing at the point where the lines emerge from the vessel, a current-return path is formed by a concentric pipe arrangement. In the long double-pipe section, which is heated to 600 C by the molten salt, the pipe temperature will be only 760 C (160 C hotter than the pipe radiating to room temperature). Line heating, of course, is not used during the fluorination.

V. ELECTROLYTICALLY HEATED VESSEL DESIGN

In electrolytic heating, heat is generated within the molten salt charge by passing electric current through the salt. Current is introduced by means of two or more electrodes immersed in the salt. This method of heating is simple and requires only low-voltage 60-cycle alternating current. Heating is efficient, since the fused salt is a moderately good conductor (resistivity of the order of 1 ohm-cm) and the solid salt is an excellent insulator.

The electrodes themselves cannot be protected by a frozen-salt layer and are subject to corrosion. However, electrodes can be made rugged enough to sustain corrosion for a reasonable length of time, and their replacement can be made relatively easily.

A Design Objectives

The overall objective of the development involving electrolytic heating was to demonstrate the formation of a controlled, thin, uniform frozen wall for a typical process scale and a typical vessel configuration. Variables considered included salt depth, gas sparging, and heat flux through the frozen wall. In addition, development of an electrical-resistance method for detection and control of the frozen wall is desirable; such a system is very attractive for remotely operated equipment.

The basic system consisted of an externally cooled metal vessel with two electrodes suspended into the molten salt charge. Design of the electrodes and their configuration was made with regard to the following features:

1. uniform salt heating, to give uniform frozen-wall thickness;
2. minimum operating temperature of electrodes for longer life;
3. overall configuration suitable for fused salt sparging and transfer operations; and
4. provision for auxiliary (nonelectrolytic) heating in initial melting of a solid (nonconducting) charge.

B. Apparatus and Procedure(5,6,7)

The container used was a dished-bottom vessel made of Monel. A diagram of the vessel and electrodes is shown in Figure 6. The inside diameter was 17.4 in. and the total inside height 52.6 in. Five external cooling zones were provided, each consisting of windings of approximately 10 turns of $\frac{3}{8}$ -in.-OD copper tubing bonded to the tank wall with copper spray metal. The height of each zone was approximately 10 in. Circulating distilled water at a constant temperature was used as coolant.

Figure 6

Schematic Diagram of Electrolytically Heated Frozen-wall Test Vessel

The electrodes are of concentric design with a 2-in. (schedule 40) nickel pipe as the outer shell. Inside this pipe, a $\frac{3}{4}$ -in.-diameter copper power lead brings the current to the closed bottom of the electrode. A $\frac{1}{4}$ -in. nickel sparge line was connected inside the electrode so that it discharged directly from the bottom. This electrode design has the advantage of applying the maximum voltage differential to the lower region of the fused salt. In this way a larger amount of heat is released near the bottom of the fused salt mass, where convection currents are effective in distributing the heat. Earlier tests with conventional solid electrodes showed difficulty in applying heat to the lower part of the fused salt because most of the heat was generated at the salt surface (the point of highest voltage differential) and no strong convection currents were set up to aid heat distribution. Independent tubular resistance heaters for startup were also located in the electrode well. The two resistance heaters in each electrode provided a total of 6 kw. Thermocouples were located in the well to

measure electrode temperature. The electrodes were mounted vertically, at a distance of 4 in. from the wall and 4 in. above the bottom of the vessel. (In later tests, the electrodes were lowered to 1.5 in. from the bottom.)

Solid sodium fluoride-zirconium fluoride salt was charged to the vessel, and initial melting was done with the internal resistance heaters to obtain a molten salt bridge between the electrodes. After this, electrolytic heating was used to complete the melting.

Argon sparging was provided through the sparge lines in the electrodes. Flows of cooling water and sparge gas were measured with rotameters. Temperatures of the electrodes and of the water coolant of the vessel were recorded during operation. Measurement of the thickness of frozen salt was taken in these tests with a large caliper through the open top of the vessel.

The electrode power was controlled by a saturable reactor by means of which power levels could be set either manually or by an automatic temperature controller. An alternative control system based on the measurement of the overall resistance of the salt wall was designed. A schematic diagram of the resistance-control system is shown in Figure 7; a low-voltage, direct-current electronic bridge circuit balanced the frozen wall resistance with any of 8 fixed-resistance points.

Figure 7

Schematic Diagram of
Power-control System
for Frozen-wall
Vessel⁽⁶⁾

The output of the controller is direct current matched to the saturable reactor control circuit. This bridge circuit provided an accurate measurement of wall resistance without interference by the ac electrolytic power. Control of the electrolytic power level gave automatic protection against removal of the salt wall for any reason. Potentially, this system might be used to control the frozen wall to a predetermined thickness. It could be applied to induction heating, also.

C. Results of Preliminary Test

An initial test of the frozen-wall vessel system was made with the electrodes positioned 4 in. above the bottom of the vessel. The salt charge was 980 lb of 40 mole percent zirconium fluoride-60 mole percent sodium fluoride, which gave a molten salt interface 38 in. from the bottom.

Measurement of the salt wall under steady conditions gave the frozen-wall profile shown in Figure 8. The thickness of the salt wall was between 1 and 1.5 in. for about 80 percent of the liquid depth (32 in.). The heavier wall at the bottom was 5 in. thick and thus extended slightly above the bottom of the electrodes.

Figure 8
Frozen-wall Profile in Initial Tests⁽⁶⁾

In order to prevent oxidation of the copper power cables joined to the top of the electrode axial bus, this copper bus was cooled at the top by a small water coil. Two sources of heat were involved, the I^2R losses generated in the bus and the heat conducted up from the fused salt. At the current level used (810 amp), the power losses generated in the copper axial bus in the two electrodes amounted to only 75 watts. Heat losses by conduction up these copper bus bars amounted to 150 watts. Possible oxidation of the copper was prevented by an argon purge of the annulus. Because power generation in the bus is not too large, the use of nickel rather than copper is recommended on the basis of oxidation resistance.

This electrode design met reasonably well the objectives stated above, and further tests were made to obtain information on the effect of process variables on the wall thickness under conditions for optimum frozen wall thickness.

D. Effects of Variables on Frozen Wall⁽⁷⁾

A series of tests was made to determine the effects of process variables on the frozen wall. The general procedure and the electrodes were the same as in previous test, but the electrodes were lowered from 4 in. to 1.5 in. from the bottom in order to reduce the frozen-wall thickness at this point.

Two salt depths, three constant-power settings, and three sparge rates were used. The unit was left overnight on a medium power level and low sparge rate. During the day the conditions of the test were set and maintained. Wall measurements were made after about 7 hr at given conditions. Any salt crust formed during this time was broken back into the molten zone to insure uniformity. Operating conditions for the eight runs are summarized in Table 5, measurements of the frozen wall in Table 6, and wall profiles in Figure 9.

During these operations, a progressively heavier crust of solid salt at the interface was noted. Because the top of the vessel was open, hydrolysis of the salt could occur and contribute to the crust formation. The salt was hydrofluorinated between Runs 4 and 5 to reconvert the oxide to fluoride.

After the wall measurements were made, the water-cooling zones were blown out (one after the other, starting at the top) to determine the effect on the frozen wall and on the crust at the surface. Finally, the electrodes were removed with the salt molten.

Table 5

HEAT BALANCE AND SPARGE RATES FOR FUSED SALT RUNS⁽⁷⁾

Run	Total Power Input (kva)	Bus Power Loss (kva)	Power Input to Salt (kva)	Zone-cooling Load ^a (kw)					Total Cooling Load (kw)	Heat loss (kva)	Sparge Rate (cfm)	Thickness of Frozen Wall (in.)
				Bottom				Top				
				1	2	3	4	5				
1	25.2	-	-	0.30	3.4	8.7	3.5	0.42	16.32	-	0.18	0.5 to 1.4
2	15.6	1.0	13.7	0.26	3.8	6.0	2.8	0.38	13.24	0.5	0.18	1.0 to 2.1
3	16.0	1.8	14.2	0.27	3.7	5.7	2.9	0.40	12.97	1.2	0.88	0.8 to 1.7
4	15.6	2.0	13.6	0.27	3.7	5.7	2.9	0.40	12.97	0.6	0.02	0.9 to 1.6
5	18.0	2.0	16.0	0.29	5.4	6.2	2.9	0.53	15.32	0.7	0.17	0.7 to 2.1
6	10.1	.9	9.2	0.21	3.4	4.2	2.1	0.33	10.24	-1.0	0.17	1.2 to 5.5
7	26.4	4.5	21.9	0.24	4.7	6.9	7.5	1.2	20.54	1.4	0.24	0.4 to 2.7
8	18.2	2.7	15.5	0.21	2.5	4.0	5.0	1.1	12.81	2.7	0.26	1.2 to 1.5

^aThe wall is cooled by 5 separate coils, each cooling a zone of approximately equal area.

Table 6

PROPERTIES OF SALT WALL⁽⁷⁾

Run	Frozen-wall Thickness (in.)				Wall Area (sq ft)	Avg Wall Heat Flux (kw/sq ft)	Wall Thermal Conductivity, BTU (hr)(sq ft)(F/ft)	Wall Resistance (ohms)	Wall Resistivity (ohm-cm)
	Min	Max	Arithmetic Average	Overall Mean ^a					
1	0.5	1.4	0.80	0.72	9.9	1.6	0.40	8,600	43 x 10 ⁶
2	1.0	2.1	1.41	1.32	9.9	1.3	0.59	47,000	120 x 10 ⁶
3	1.0	1.7	1.21	1.14	9.9	1.3	0.51	53,000	120 x 10 ⁶
4	1.0	1.7	1.24	1.18	9.9	1.3	0.52	78,000	210 x 10 ⁶
5	0.7	2.1	1.13	0.98	9.3	1.6	0.54	1,600	5.6 x 10 ^{6b}
6	1.2	5.5	2.30	1.72	9.1	1.1	0.65	8,900	17 x 10 ⁶
7	0.4	2.7	0.88	0.64	13.6	1.6	0.35	2,900	23 x 10 ⁶
8	1.0	1.5	1.30	1.28	13.3	1.0	0.42	12,000	46 x 10 ⁶

^aReciprocal of the reciprocal average wall thickness, in.

^bA minimum value of 2 x 10⁶ was observed during HF additions.

Figure 9
Frozen-wall Cross Sections⁽⁷⁾

1. Results of Wall Measurements

As can be seen from the frozen-wall profiles in Figure 9, the thickness of the frozen wall was maintained quite uniformly in the range from $\frac{1}{2}$ to 1 in. on the wall and from 1 to $1\frac{1}{2}$ in. on the bottom with a power level of approximately 1.5 kw/sq ft of frozen wall. The dependence of wall thickness on power level can be seen in Figure 10.

Figure 10

Overall Mean* Wall Thickness at Various
Wall Heat Fluxes⁽⁷⁾

*(See text for explanation)

Lower power densities resulted in thicker walls, particularly at the bottom. The overall mean wall thickness is defined by heat transfer equations in which total heat flow is obtained by summarizing the flow in separate zones of different wall thickness Δx_i . The following equation was derived for the total heat flux:

$$q = k(\Delta T)(A_i n) \left[\frac{\sum_{i=1}^n \left(\frac{1}{\Delta x_i} \right)}{n} \right]$$

$$= kA \left[\frac{\Delta T}{\text{overall mean wall thickness}} \right]$$

where k is the thermal conductivity, ΔT is the temperature difference between the molten salt and the cooling water, A_i is the area of one zone, n is the number of zones, and A is the total zone area assuming all zones are of equal area. Wall thickness and heat flux are generally consistent with those obtained in the induction-heating tests described in Table 4.

A summary of heat balance and sparge conditions for the eight runs is given in Table 5. Maximum heat pick-up was found in the middle cooling zones. Values of the input to the salt are the difference between the kva supplied and losses in the bus conductors. In Run 1, the bus losses were high because of a poor connection, and are not reported. The heat losses unaccounted for in the cooling water varied from very low values to about 10 percent of input power.

Power density appeared to be the controlling variable with respect to wall thickness, as can be seen from Figure 10. The variation in salt levels and sparge rate did not appear to have any definite effect (see Table 5). The salt levels used were 26 and 36 in., and the sparge rates ranged from 0.01 to 0.5 ft/min, based on the total cross-sectional area of the vessel. The sparge was divided between two $\frac{1}{4}$ -in. open-tube sparge lines, one in the bottom of each electrode.

2. Electrical Resistance Measurement of Salt Wall

Measured values of overall wall resistance varied from 1600 to 78,000 ohms for the operating conditions noted. These were obtained with a 30-volt dc bridge circuit, with the positive potential at the vessel wall and the negative at the electrodes. The opposite polarity was tried initially, but it resulted in false low readings, probably because of deposition of zirconium metal needles on the salt wall. A summary of measured electrical resistance and calculated values of electrical and thermal conductivities of the salt wall is given in Table 6.

As shown in Table 6, considerable variation in wall resistivity occurred during the tests. Pure salt near room temperature has a resistivity of the order of 10^8 ohm-cm. In Runs 1 through 4 the resistivity calculated from overall resistance measurements increased from 4×10^7 to 2×10^8 ohm-cm. Between Runs 4 and 5, the salt was sparged with 25 lb of hydrogen fluoride. An abrupt decrease in resistivity occurred with the hydrofluorination. The lowest resistivity, 2×10^6 ohm-cm, was observed during sparging. (In this period an oxygen analysis of the salt showed 0.6 percent in the fused salt and 3 percent in the solid at the top.) In subsequent runs, in which the argon sparge was resumed, the resistivity steadily increased to about 5×10^7 ohm-cm. Because of the small oxygen content of the salt and because of parallel effects of resistivity changes and hydrofluorination, it is indicated that the hydrogen fluoride content of the solid salt wall is a major determinant of wall resistance. With fluorination, however, such variations would not be expected.

Also in Table 6 are values of thermal conductivity calculated from the heat transfer equation, obtained with the use of the overall mean wall thickness as previously defined. These values are consistent with those presented in the literature.

At the conclusion of the tests, the frozen wall was melted completely off the side wall and bottom, by continuing electrolytic heating after shutting off the external cooling. The crust at the interface, however, was not removed, because of the combination of high heat losses for the open-top test vessel and the absence of direct heating of the solid salt. External heating would be required for remelting the crust.

E Corrosive Attack on Electrodes

After about eight days of continuous operation, the vessel was shut down and the salt removed. The dimensional changes of the electrodes were measured. Attack consisted of surface irregularities or shallow pits concentrated on the surfaces of the electrodes that faced each other. The left electrode had pits ranging up to 40 mils in depth, and the right electrode had a few pits as deep as 80 mils. The absence of interface attack was probably due to a surface crust at the electrode, which was cooled at the top. Considerably more attack was noted on one of the electrodes, but no reason for this was evident.

The above attack was sustained in early tests, before the final series of 8 runs described above. In these final runs, the same electrodes were used, although they were rotated so that the thicker sections were at the point of maximum current density. At the end of the final test period, the electrodes were removed with the salt molten. It was then found that electrode attack had continued and, in fact, several holes had appeared in one electrode. From the exposure times involved, the rate of attack was the same as observed before, namely, 10 mils/day at the path of maximum current density. The penetration of the wall of the electrode by molten salt had no noticeable effect on the testing operations.

F. Further Considerations for Plant Application

Since 1000-lb salt charges were used in these electrolytically heated vessel tests, the equipment represents full plant scale. The power supply and cooling system are also considered suitable for plant use. All-nickel electrodes are recommended for maximum dependability. Although further work on optimizing electrode life and in controlling crust formation is desirable, the general design appears feasible for plant use. The most serious objection is the probable necessity of electrode replacement on a weekly or monthly basis.

ACKNOWLEDGEMENTS

Valuable assistance in construction and operation of the test equipment was given by J. Gates and W. Murphy of the Chemical Engineering Division, and B. Bydal, a student aide from the University of Illinois. W. Voss, Central Shops machinist assigned to the Chemical Engineering Division, fabricated the very symmetrical and compact nickel cooling coil for the induction-heating tests.

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